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Technical Report No. 32-548

# Metallurgical Examination of Development-Type Thermionic Power Converters

E. C. Bernett

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JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
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#### **ABSTRACT**

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Examinations were carried out on a number of thermionic power converters (diodes) after they had been tested to failure. The purpose was to check for failure causes and substandard material or workmanship.

Some components of the early-model diodes showed very poor machine finishes; however, there was a noticeable improvement in the later models. The braze joints (particularly the metal—ceramic seal) continue to show a marked variation in structure from model to model, indicating a lack of process control in this area. Heavy foreign deposits were observed on the collectors of two diodes, and there was an intergranular cesium attack on two emitter sleeves. The exact nature of these two effects could not be established, but the evidence indicates they were associated with impurities in the cesium and with poor control of the test atmosphere.

RUTHOR

#### I. INTRODUCTION

A program to develop thermionic power converters suitable for use in space vehicles is described in SPS 37-21, Vol. IV.¹ Four development converters, all from the same manufacturer,² were submitted to the Materials Research Section of the Jet Propulsion Laboratory (JPL) for metallurgical examination. Each of the converters had previously been test-run to failure or until the output had slumped badly. The purpose of the metallurgical examination was to check for failure causes and substandard material or workmanship.

The converters involved in this examination represent three development models, Series V, VI, and VII. The total run times and other data on each unit are given in Table 1.

Table 1. Test-run data

Diode Serial Tested by No.		Time to Power failure, hr output		Failure cause	
Vb	Supplier	86	Average	Cesium leak	
Vc	Supplier	240	Average	Slumped	
VI	Supplier and JPL	150ª	Very high	Slumped and leak	
VII	Supplier	50	Average	Cesium leak and slump	

All of the units listed above were of the same basic design; Fig. 1 and 2 show an external view and a cross-section, respectively. These are views of a Series V diode with a flat (external) face on the emitter. The faces on diodes VI and VII were concave, and the surfaces were serrated for better heat transfer.

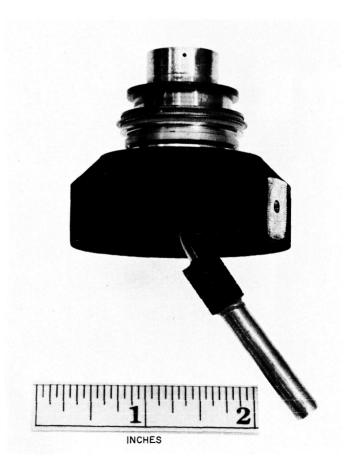


Fig. 1. External view of thermionic diode, Serial No. Vb

<sup>&</sup>lt;sup>1</sup>Smith, A. H., Rouklove, P., and Brozdowicz, Z., "Power Sources," Space Programs Summary No. 37-21, Vol. IV, Jet Propulsion Laboratory, Pasadena, California, June 30, 1963, p. 20.

<sup>&</sup>lt;sup>2</sup>Thermal Electron Engineering Co., Waltham, Mass.

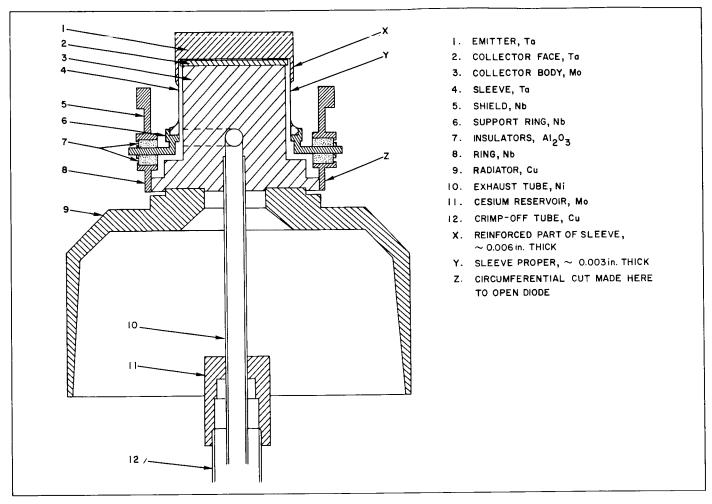


Fig. 2. Cross-section of diode. The same design was used for the Series V, VI, and VII diodes

### II. VISUAL AND MACROSCOPIC EXAMINATION

#### A. Diode Vb

The outstanding external feature of diode Vb at first glance was the apparent coating of copper on the alumina insulator (see Fig. 1). It seemed that this would produce an electrical short; however, a continuity check was negative. The other notable features were (a) the large grain size and prominent thermal etching on the emitter (Fig. 3) and (b) the circumferential band of dark spots on the sleeve (Fig. 4). The spots were later found to be points of cesium leakage. The grain coarsening in the emitter is more apparent in the sectional view in Fig. 5.

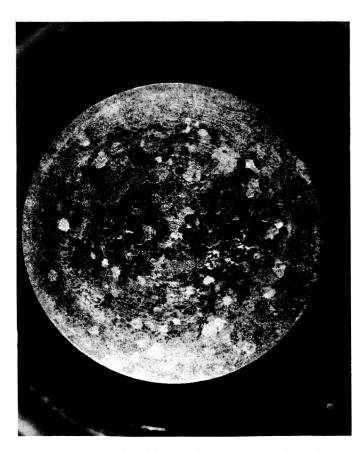


Fig. 3. Thermal etching of the diode Vb emitter face (heated surface). Mag, 5X

The diode was cut open (at point Z in Fig. 2) to permit examination of the inside. A peculiar greyish "etch" pattern was noted on the working faces of the emitter and the collector (Fig. 6). There was insufficient buildup of foreign matter to permit any spectrochemical analysis.

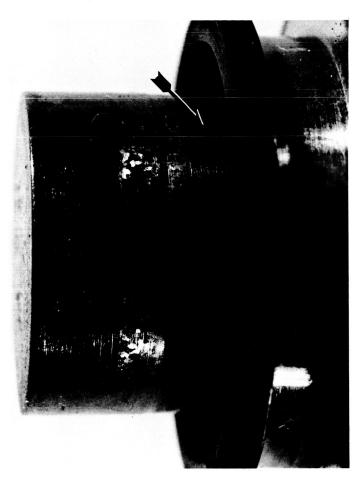


Fig. 4. External view of emitter—sleeve portion of diode Vb. Note circumferential band of dark spots on sleeve. Mag, 5X

During a subsequent sectioning operation, the sleeve cracked in half. The completely brittle fracture ran through the belt of dark spots visible in Fig. 4 and extended around the full circumference.

The last feature of note in the visual examination of this diode was the poor machining finish in various places and especially on the inside surface of the sleeve. The tool marks here were as much as 0.0015 in. deep, and since the unreinforced portion of the sleeve is only 0.0035 in. thick, the actual metal thickness at the bottom of the tool marks was only 0.002 in.

#### B. Diode Vc

The outward appearance of diode Vc was much like that of diode Vb except for a more severe degradation

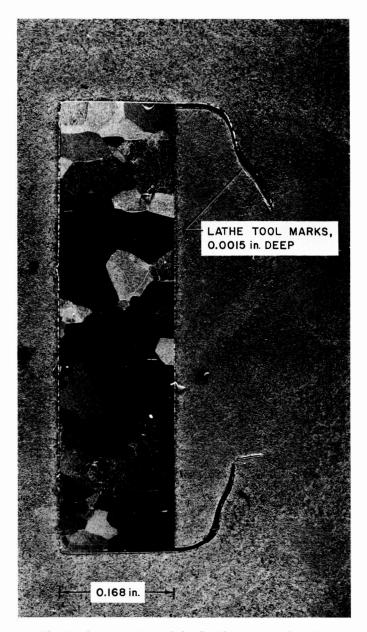


Fig. 5. Cross-section of diode Vb emitter, showing coarse grain size and deep tool marks

of the heated surface of the emitter (Fig. 7). The grain size was larger, and some grains were later found to extend through the full 0.167-in. thickness of the emitter (Fig. 8). The grain boundaries, which were very prominent, were opening, and one grain had become separated and had fallen out. Also, there were a number of small rounded protrusions on the heated surface of the emitter; these looked like beads of previously molten metal.

When this diode was cut open, it was immediately noted that the conditions of the emitter and collector



Fig. 6. "Etch" pattern on working faces of emitter and collector, diode Vb

faces were much different from those in diode Vb, described previously. The emitter in diode Vc was completely clean and bright, and the collector was covered all over with a uniform, dark-grey, soot-like coating. There was no trace of any "etching" of the emitter as noted on diode Vb.

The internal and external machining finishes on this diode were much better than those previously observed on diode Vb.

#### C. Diode VI

This diode was one of five in a generator assembly that had operated normally for 150 hr. At this time the generator was accidentally dropped some five feet onto the concrete floor during a relocation in the test cell. The whole generator was disassembled and each diode was checked separately. The diode being examined here operated properly at low power levels but when operation at maximum was attempted there was a sudden drop in

output. At the same time there was some fogging of the vacuum bell jar (normally indicative of a cesium leak). A close external examination of the diode failed to reveal any evidence of leakage such as that noted on diode Vb (Fig. 4) and diode VII, described later in this report. On the whole, diode VI appeared to be in perfect condition; externally the emitter was perfectly clean and not degraded, the machine finishes were excellent, and the braze joints looked sound.

The diode was then cut open and the internal surfaces were examined. The emitter face was clean all over. The tool marks were prominent across the full face and the grain structure was just distinguishable. The grains were equiaxed and the average size was about 0.040 in. Closer observation of the emitter face showed numerous clean pits just visible to the naked eye. The condition of the collector face was markedly different from that on diodes Vb and Vc, described previously. The collector face on diode VI was clean except for a number of small dark spots (the largest being about 0.02 in. across). Also present on this face were numerous very small bumps. These



Fig. 7. Heavy thermal etching of the diode Vc emitter face (heated surface). Note that one grain has fallen out. Mag, 5X

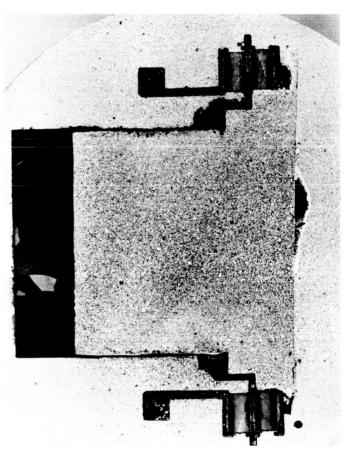


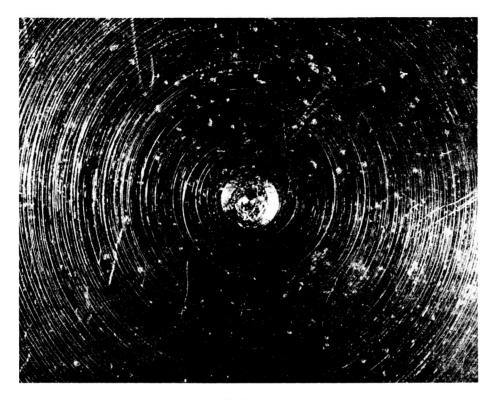
Fig. 8. Section through emitter—seal portion of diode Vc. Mag, 4X

looked like metal splatter one normally sees near arc welds. Views of the emitter and collector faces are shown in Fig. 9.

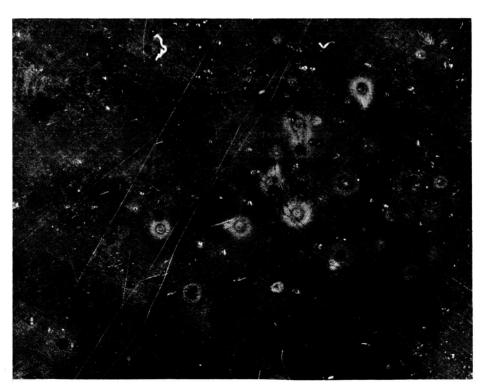
#### D. Diode VII

This unit developed a cesium leak in the tantalum sleeve after a relatively short total test time of about 50 hr. The diode had been cut open by the supplier (see Fig. 10). The heavy dark deposit on the collector face is plainly evident, as is the point at which the cesium leak occurred. A closeup of this point is shown in Fig. 11 (external view) and an internal view is shown in Fig. 12. This grain boundary attack (Fig. 12) was confined to a belt approximately 0.1 in. wide and extended the full circumference of the sleeve. The sleeve was brittle in this zone.

The working surface of the emitter was clean except for a smudge of deposit (Fig. 10) which had rubbed off the collector after the unit had been cut open. Of the



**E**mitter



Collector

Fig. 9. Condition of working surfaces of emitter and collector on diode VI. Mag, 10X

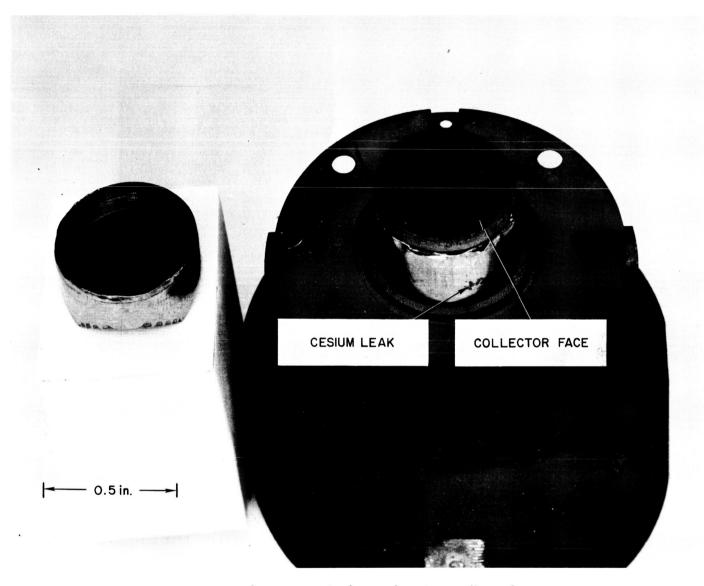


Fig. 10. Diode VII, as received. Note deposit on collector face

four units under examination here, the collector face on this diode was the dirtiest. A dark grey powdery deposit about 0.003 in. deep was present on the whole surface. The outer material could be readily scraped off; however, the last 0.001-in. layer (next to the metal) was highly adherent.



Fig. 11. Cesium leak area on sleeve of diode VII, outside view



Fig. 12. Cesium leak area on sleeve of diode VII, inside view

#### III. DIMENSIONAL AND SURFACE-FINISH CHECKS

Wherever possible, dimensional and surface-roughness checks were made on some of the critical parts and areas of each diode. The pertinent figures are listed in Table 2. The roughness values, shown in microinches (rms), were determined with a G.E. Surface Roughness Gauge.

A levelling fixture has just recently been acquired, and it is now possible to make flatness checks on the working surfaces of the collector and emitter. Measurements on diode VI showed these mating surfaces to be flat within 0.0001 in.

Table 2. Dimensional and surface-roughness data

Item	Diode Vb	Diode Vc	Diode VI	Diode VII
Tantalum sleeve thickness, in.	0.0035	0.0025	0.0023	0.0030
Tantalum sleeve thickness (reinforced part), in.	0.0065	0.0060	0.0062	0.0060
Collector face diameter, in.	0.6265	0.6265	0.6275	0.6270
Emitter surface roughness, $\mu$ in.	75	32	32	32
Collector surface roughness, $\mu$ in.	8	_a	8	_•
Tantalum sleeve surface roughness (inside), $\mu$ in.	63	32	16	16
Tantalum sleeve surface roughness (outside), $\mu$ in.	32	32	16	16

aThese surfaces were covered with sooty deposit; therefore, the finish was not checked.

#### IV. DYE-PENETRANT EXAMINATIONS

Dye-penetrant crack-detection tests were made on the emitter assembly after each diode was cut open. The developer solution was brushed onto the outside surfaces and allowed to dry. The dye was then applied to the inside of the emitter assembly. The unit was examined periodically for at least 24 hr to check for any dye seepage. On diode Vb, an immediate penetration of the dye occurred about the full circumference of the tantalum sleeve in the zone where the dark spots were previously noted (Fig. 4). The checks on diodes Vc and VI were negative; that is, no leaks were found. On diode VII, a very faint indication of leakage was observed at the point

on the sleeve where some discoloration had previously been noted (Fig. 10).

Diode VI had apparently sprung a leak towards the end of its test life, as evidenced by fogging of the vacuum bell jar, yet no leak was found by the dye test. Of course, the leak may have been located in the cesium reservoir area, and this portion was not leak-checked. It is also possible that a small crack or pinhole was present in the sleeve assembly but was closed tight at room temperature. At the operating temperature, however, a small defect could open and result in excessive leakage.

#### V. X-RAY AND SPECTROCHEMICAL CHECKS

X-ray diffraction and spectrochemical checks were carried out on the dark-colored soot-like deposits found on the collector face of diodes Vc and VII. The X-ray checks were carried out on the deposited material *in situ*, using a General Electric XRD-3 diffractometer, and also on scrapings, using a Norelco powder camera. All the checks

showed that the deposit was primarily tantalum. There were also indications of some tantalum nitrides; however, this could not be positively established.

Semiquantitative spectrographic chemical analyses were made on microsamples (5 to 15 mg) of the deposits

Table 3.	Composition of	deposits on co	llector faces

	Diode	Diode VIIª, %				Diode	Diode VIIª, %		
Element	Vc, %	1	2	3	Element	Vc, %	1	2	3
Tantaium	84.00	67.00	93.00	94.00	Titanium	0.02	Nil	Nil	Nil
Silicon	0.06	0.07	0.17	0.10	Silver	0.01	Nil	Nil	Nil
Iron	0.12	0.01	0.15	0.11	Cobalt	0.01	Nil	Nil	Nil
Magnesium	0.01	0.01	0.02	0.02	Aluminum	0.01	Nil	0.10	0.10
Manganese	0.01	Nil	Nil	Nil	Calcium	0.01	0.02	0.10	N.A.
Nickel	0.04	Nil	Nil	Nil	Chromium	Tr.	Nil	Tr.	Nil
Molybdenum	0.01	0.05	0.15	0.10	Barium	Nil	0.01	Nil	Nii
Tin	0.04	Nil	Nil	Nil	Cesium	N.A.°	0.25	2.80	1.70
Copper	Tr. <sup>b</sup>	0.01	0.04	0.03	Other	Nil	Nil	Nil	Nil

<sup>&</sup>quot;Sample 1 from diode VII was the loose outermost layer of the deposit on the collector face. Sample 3 was the dense, tightly adherent material next to the tantalum face, and Sample 2 was an intermediate layer.

<sup>&</sup>lt;sup>b</sup>Trace—less than 0.005%.

Not analyzed.

scraped from the collector faces. The results are listed in Table 3.

It should be pointed out that the tantalum values shown in Table 3 may be inaccurate. There is no doubt

that the principal constituent of the deposits is tantalum. However, the small sample size, the unknown particle size, and the degree of oxidation, if any, are all factors that can cause a significant error in the true tantalum content.

#### VI. MICROSCOPIC AND MICROHARDNESS CHECKS

Microscopic examinations were made on metallographic sections of the emitters, sleeves, metal-ceramic seals, various braze joints, and miscellaneous other areas of each diode. A number of interesting features that were noted are described below.

- 1. There was a particularly noticeable difference in the structure of the metal-to-ceramic braze in the Series V, VI, and VII diodes, as may be seen in Fig. 13, 14, and 15, respectively. In the case of diode Vb (Fig. 13), there was a very heavy intergranular diffusion of the brazing filler into the niobium. This had embrittled the niobium, as evidenced by the cracks through the metal along the region where the alumina had broken away when the sample was cut. The diode VI braze (Fig. 14) showed no evidence of any gross diffusion of the filler metals into the niobium, as was observed in the previous unit. In diode VII, the braze filler had apparently segregated into nickel- and copper-rich zones (Fig. 15). Further information on the metal-ceramic seals is given later in the sections on microhardness and microprobe studies.
- 2. As was mentioned previously, one of the striking external features of these diodes was the coarse grain size of the emitter and the severe intergranular cracking of the heated surface. Cross-sectioned views of the diode VII emitter at low and high magnification are shown in Fig. 16 and 17. The intergranular voids are concentrated near the heated surface; however, one void may be observed more than three-quarters of the way through the emitter. In units that are expected to operate for very long times, this might be a major problem.

3. Cesium leaks in the sleeve had developed in two of the four diodes being examined here. Metallographic specimens were therefore prepared from the sleeves of

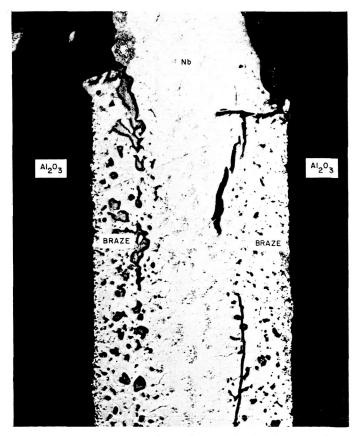


Fig. 13. Alumina-to-niobium braze, diode Vb. Note that braze joint on the right had separated during sectioning. Mag, 100X

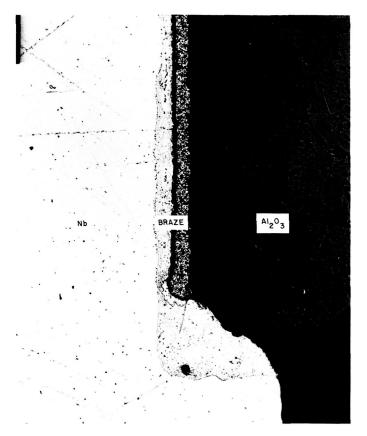


Fig. 14. Alumina-to-niobium braze, diode VI. Mag, 100X

all the diodes in an attempt to determine why some developed leaks. Two views through the defective areas are shown in Fig. 18. The cracks, which originate from the inside surface of the sleeve, are intergranular and do not spread away from the boundary. This is more evident in the high-magnification view of one attacked boundary in Fig. 19. The reason for this attack could not be positively established.

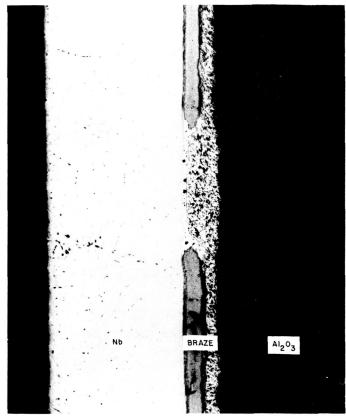


Fig. 15. Alumina-to-niobium braze, diode VII. Mag, 100X

4. There were seven braze joints on these diodes (exclusive of the ceramic seal). The metallographic examination of these joints did not reveal any major defects or potential problem conditions.

The specimens prepared for the microscopical examinations were also used for the microhardness studies with a Leitz Miniload machine. A Knoop diamond indentor

Table 4. Knoop microhardness data

<b>D</b> : 1	Tantalum		Tantalum sleeve		Niobium components		Metal-ceramic	_
Diode	emitter	Near emitter	Midzone	Near end	Parent metal	Near braze	braze filler	Remarks
Vb	250	240	470	155	225	600	534	Sleeve leak
Vc	170	170	170	170	175	300	534	No leak
VI	140	165	192	170	130	180	600	No leak
VII	250	260	330	260	175	175	1,600	Sleeve leak

Note: The table shows average hardnesses as measured with loads of 15 to 100 g. The values in the metal-ceramic braze filler column are for the hardest phase present.

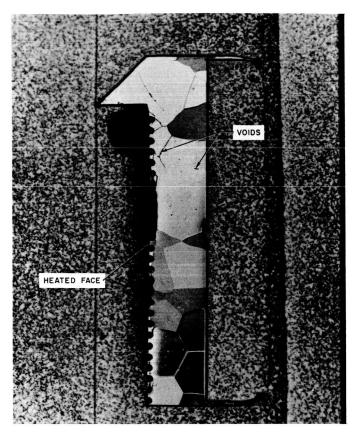


Fig. 16. Section through diode VII emitter. Note coarse grain size and intergranular voids. Mag, 10X

and various test loads ranging from 15 to 100 g were employed. Checks were made on the tantalum sleeve and emitter, on the metal parts near any braze joints, and on

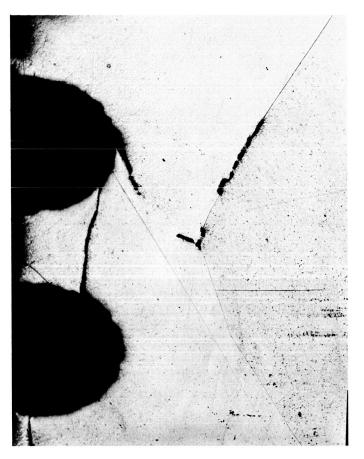
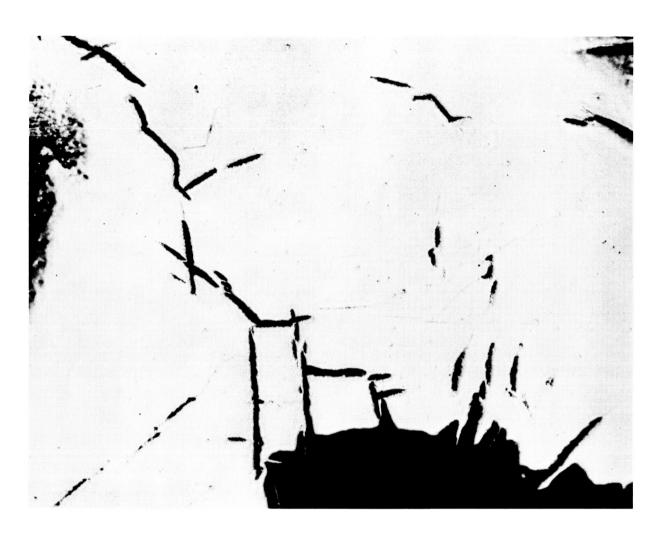


Fig. 17. Intergranular voids in the emitter from diode VII. Mag, 100X

the braze filler metals. The measured hardnesses are listed in Table 4.



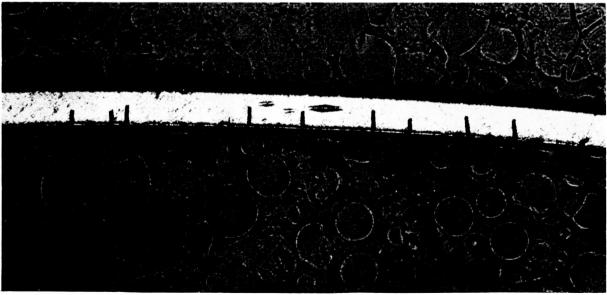


Fig. 18. Grain boundary attack of tantalum sleeves. The top photograph shows a side view of the sleeve from diode VB and the bottom photograph shows a cross-section of the sleeve from diode VII. Mag, 150X



Fig. 19. Grain boundary attack on sleeve from diode VII. Mag, 1,000X

#### VII. X-RAY MICROPROBE EXAMINATIONS

The previously described examinations had revealed a number of instances where gross diffusion or segregation of certain elements had occurred. This was particularly noticeable in the metal-ceramic braze joints. In the case of the Series V diodes there was a heavy diffusion of braze filler into the niobium support ring (Fig. 13). X-ray microprobe checks showed that both copper and nickel had diffused intergranularly into the niobium support ring, causing the hardening and embrittlement of this component. In the Series VII diode there was pronounced segregation along the metal-ceramic braze joint (Fig. 15). A high-magnification view of one area of this joint is shown in Fig. 20. The microprobe checks of this area showed that the light-colored phase (previously found to be very hard, i.e., 1,600 Knoop) was niobium base with 35% nickel, 6% copper, and 4% molybdenum. The darkcolored phase was principally copper, and the mottled material was the molybdenum metallizing. The metallized zone also contained amounts of titanium ranging from 1 to 14%.

Microprobe analysis was also done on the corrosion product that was extruded from the grain boundaries of the diode VII sleeve (Fig. 12), and a high percentage of cesium was found. Cesium could not be detected on the parent tantalum away from the boundary region.

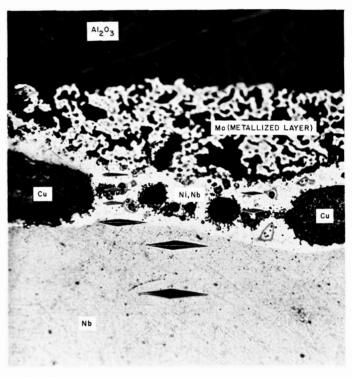


Fig. 20. X-ray microprobe and Knoop microhardness survey through the metal—ceramic braze on diode VII. Mag, 500X

#### VIII. DISCUSSION

Although there were no metal-ceramic seal failures in the diodes examined here, there were particularly pronounced variations in the structure and hardness of the seal brazes, and this nonuniformity could develop into a trouble spot. The gross diffusion of braze filler into the niobium support ring on the Series V diodes (Fig. 13) indicates that these units were badly overheated during the brazing cycle. There was no indication of excessive overheating on the VI and VII diodes; however, the braze joints were again quite different structurally (Fig. 14 and 15). Evidently there continues to be some lack of process control in the metal-ceramic seal brazing operation.

The thin tantalum sleeves are critical elements on these diodes, as evidenced by the fact that two of the four failed as a result of cesium leaks in this area. The increased hardness of the sleeves in the cesium-attacked zone would indicate that contamination is involved. It is possible that this zone getters interstitial elements from the vacuum atmosphere during operation. These elements would tend to segregate at the grain boundaries, and when the concentration reached a certain level, the boun-

daries would become prone to cesium attack. There is now hope that X-ray microprobe techniques that will permit analysis for oxygen, nitrogen, and carbon will soon be available. With this information it should be possible to establish the reason for the cesium attack.

The sooty dark deposit on two of the collector faces was found to be tantalum with traces of other elements. There is little doubt that the tantalum came from the hot emitter surface; however, it could not be determined why the deposit formed on two collectors and not on the others. It is possible that this is due to the operating condition of a particular diode or perhaps to some impurities that are present in the cesium or are introduced during the diode-charging operation. A close and continuous check of these factors in the future would be helpful.

With regard to the machining finishes on these units, Table 2 shows a definite trend. The finishes on diodes VI and VII were much better than those on the earlier V series. Consistently good machine finishes are certainly desirable on critical devices such as these diodes.

#### IX. CONCLUSIONS

- 1. Two of the diodes examined (i.e., Serial No. Vb and VII) failed as a result of cesium leaks through intergranular cracks in the tantalum sleeve. The slump in the power output from diode Vc was apparently due to formation of the deposit on the collector. The slump of diode VI was probably due to loss of cesium; however, the location of the leak could not be determined.
  - 2. The intergranular cracking of the sleeves (diodes Vb
- and VII) was associated with severe embrittlement. The embrittlement is most probably due to gettering of interstitial elements from a poor vacuum environment during test.
- 3. The variations in the appearance of the metal-toceramic braze zone and the large differences in the hardness of the filler material indicate a lack of process control during brazing.